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## Approaches to Thermoelectric Standardization

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### 26.1 Introduction

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Increasing scientific collaboration between national and international laboratories and also with industry has resulted in an increased awareness of a need for accurate data comparison, including confidence in assessing quality and reliability. The importance of standardization in measurements cannot be overvalued, since without it the commercialization of research ideas and devices is threatened.

Future progress in thermoelectric materials and applications development and in thermoelectric device technology requires accurate and reliable measurement of the properties of materials and devices. Thermoelectric materials find increasingly wider application for energy conversion, Peltier cooling, sensors, devices, and systems, with a dynamically growing market and production output.

Materials and device characterization plays a key role in thermoelectric research, since evolutionary improvement of materials and systems requires a continuous feedback cycle between preparation and characterization to assess the influence of variation in materials composition, preparation routes, and parameters on the achieved thermoelectric (TE) performance (for example, functional properties and figure-of-merit of materials, efficiency, coefficient of performance, or sensitivity of devices).

Thermoelectric materials characterization includes commercial and noncommercial techniques for measurement of the Seebeck coefficient  $S$ , electrical  $\sigma$ , and thermal conductivity  $\kappa$ , thermoelectric figure-of-merit  $Z$ , thermal diffusivity, and specific heat, Hall coefficient (to determine charge carrier concentration and carrier mobility), and in addition the galvanomagnetic and thermomagnetic properties. Thermoelectric characterization also includes spatial monitoring of the thermoelectric properties for evaluation of materials functional homogeneity, and evaluation of TE device parameters and performance, for example, of thermogenerators, Peltier coolers, heat pumps, and TE sensors.

Simultaneous measurement of basic properties ( $S$ ,  $\sigma$ ,  $\kappa$ ,  $Z$ ) has turned out to be an efficient route towards accurate and reliable results. Special facilities and techniques have been developed to evaluate thin films, TE microsystems, and nanomaterials and to make measurements at high temperature, under atmosphere, or in the nonsteady-state.

Thermoelectric measurements technology, although used on a laboratory scale for decades, has yet to achieve a level of commercial availability and distribution. There is an increasingly growing demand for such technology due to the growing significant thermoelectric community within Europe, US, Japan, China, and other regions worldwide. The number of laboratories active in this field has grown steadily, stimulated by the development of scientific innovations in this field during recent years. A poll in 2003 has identified over 600 scientists active in thermoelectric research in Europe alone. This encouraging progress, however, is being hampered in its commercialization to some extent by the lack of ready-to-use accurate measurement facilities.

Standardization is defined as causing “to conform to a standard.” This includes conformity of measuring devices to standards of metrology, such as calibration with standard reference materials. In a wider sense, standardization means implementation of common techniques, and includes customized procedures and devices as well as common availability of technical equipment in order to set guidelines and measurement procedures to guarantee agreed accuracy levels of results.

Customization of thermoelectric measuring technology would open methodologic overlaps to lucrative activities such as the large and growing scientific and technological field of electroceramics, electronic wafer-based technology, crystal growth of electrical functional materials and so on. This in turn would feedback lead to the development and proliferation of thermoelectric techniques. The growing spectrum of new thermoelectric applications has stimulated increasing interest among major industries including automotive and energy suppliers. Standardization and customization in thermoelectrics appears as a prerequisite to entering stable interaction with these large markets which would establish a growing demand in commercial apparatus and routine thermoelectrics methodology. At present, reference materials and methods for TE properties measurement except for metallic thermocouple wires and thermal conductivity are not available. In addition, thermal conductivity standards are not suitable as standards for other thermoelectric properties, since these are generally outside the normal range of values of electrical conductivity and, most importantly, the Seebeck coefficient. A priority requirement is that a high- $Z$  material should be available as a standard reference material for the figure-of-merit.

### 26.1.1 Scope of Thermoelectric Standardization

The driving force for international integration in the field of thermoelectric standardization is the necessity to improve the reliability and availability of thermoelectric measurement facilities. Research groups are mostly small, operating mainly in-house built TE measuring facilities. Often, TE measuring apparatus are built to a specific design for a certain type and shape of sample. Generally, these apparatus do not reach a level of common operability and are not sufficiently documented. Thus, often the successful utilization of these facilities discontinues after its builder has moved on to different employment. International interaction, coordination, and clustering between research groups or companies are required for standardization and customization of TE measurements. The participants would take advantage from an improved TE infrastructure. One of the targets of such collaboration would be to transfer knowledge in TE evaluation from an academic level to broad common access.

A spin-off from the FP5 research project NanoThermel (“Nanoengineering of high-performance thermoelectric materials,” 2001–2003) has been the first institutional step in Europe to attain TE standardization in the EU. The axis DLR Cologne, Germany — NEDO Cardiff University, U.K. — University of Århus, DK for comparative TE measurements has been established.

In this context standardization aims at comparability of results obtained in different laboratories, reproducibility of measurements, quantification of the certainty of measurements, especially of

performance parameters ( $ZT$  values and apparatus performance). In order to correctly identify areas where future effort of thermoelectrics development should focus, a system for approving outstanding results on material performance should be established.

Calibration and evaluation of characterization facilities is an essential instrument in this process. These provide basic data on reproducibility of an individual apparatus as well as a comparison with other apparatus with similar or dissimilar principle of operation. Those comparisons will assist to reveal and identify sources of systematic errors, to identify most reliable techniques and devices, and finally to produce the necessary technical background to establish standard reference materials.

Instruments in this process are:

- Repeated measurement on an apparatus with and without remounting the sample.
- Intralaboratory and interlaboratory tests.
- Round-robin measurements to compare performance of methods and apparatus.
- Establishing reference facilities in selected accredited laboratories.
- Establishing national and international certified standards in reference materials, techniques, and apparatus to increase the accuracy and reliability of measurement.

### 26.1.2 Basic Aspects of Standardization

General basics on metrology are, for example, accessible from Ref. [1]. Guidelines on expression of uncertainty in measurements are given in Refs. [2,3]. Vocabulary and symbols for statistics which are relevant for evaluation of experiments are available in ISO 3534-1.<sup>4</sup>

Reference materials are central objects of measurements standardization. As formulated in Ref. [5], “reference materials are classified as primary, secondary, and tertiary reference materials. Some materials have its properties certified by, or its certification is traceable to, an authoritative national or international organization, agency or laboratory. These materials are called *certified reference materials*. When available, these materials have advantages over uncertified reference materials because source, lot, purity, and uncertainties in the property value are defined.

A reference material should satisfy the following requirements: it must be easily obtainable in a pure state, stable, nonhygroscopic, non volatile, easily made into a suitable form for the measurement, and physiologically harmless. In addition, reference materials must not react with the instrument material, the surrounding atmosphere, and photoreactions must not occur.”

Worldwide development of generic standards and related activities is handled by the International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC), the latter responsible for international standardization in the fields of electricity, electronics, and related technologies.

Worldwide standardisation and records to the International System of units (SI) are maintained by the Bureau International des Poids et Mesures (BIPM), France. Here, national standards and references to fundamental measurement properties (such as length, voltage, and mass) are compared against BIPM’s own fundamental standards, either in house or at customers’ premises via “traveling standards.” This assures that accredited laboratories therefore maintain a global agreement with each other.

Within Europe, the needs of standardization of different industries are handled by the European Committee for Standardization (CEN) by the action group CEN/STAR. STAR focuses on research and development required for the standardization process; its main objective is to increase cooperation between standardizing bodies and researchers and also to interface with the European Commission as well as other bodies funding research in Europe for the benefit of standardization.

National measurement institutes exist throughout Europe, for example, Laboratoire National d’Essais (LNE) in France, reference laboratory of the French Bureau National de Métrologie (BNM), the National Physical Laboratories (NPL) as the United Kingdom’s accredited national standard laboratory, Physikalisch-Technische Bundesanstalt (PTB) in Germany, Istituto Elettrotecnico Nazionale Galileo Ferraris (IEN), and the Istituto di Metrologia “Gustavo Colonnetti” (IMGC) within Italy. NPL’s and

many others' quality management system has been registered to ISO 9001:2000 for scientific R&D and the provision of internal services.

One mechanism to achieve quality and traceability to national and international standards is that of standard reference materials (SRMs). As defined by ISO Guide 30-1992 (E),<sup>6</sup> a reference material (RM) is "a material of substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials." The National Institute of Standards and Technology (NIST), formerly the National Bureau of standards (NBS), is based within the U.S. and offers for sale over 1300 different materials through its standard reference material program. The majority of these materials are certified RM, well characterized materials produced in quality for the purpose of improving measurement science. Certified values are obtained by one or more of the following measurement routes: (i) a reference method previously validated, (ii) two or more independent reliable measurement methods, and (iii) a network of technically competent laboratories thoroughly knowledgeable with the material tested.

### 26.1.3 Interlaboratory Testing

Interlaboratory comparison tests are defined by the National Conference of Standards Laboratory (NCSL International) in the document NCSLI RP-15. The following categories are defined:

*Proficiency Testing (PT)* — "The determination of laboratory performance by means of comparing and evaluating calibrations or tests on the same or similar items or materials by two or more laboratories in accordance with predetermined conditions."

*Interlaboratory Comparison Program (ILC)* — "Provide organisation, performance and evaluation of calibrations or tests on the same or similar items or materials by two or more laboratories in accordance with predetermined conditions."

*Round-Robin Test Program* — "A technique of comparing laboratories in which each laboratory is matched in turn against every other participating laboratory."

*Measurement Assurance Program (MAP)* — A program for measurement processes that provide "information to demonstrate that the total uncertainty of the measurements (data) is sufficiently small to meet requirements. The total uncertainty of the data includes both random and systematic components of error relative to national or other designated standards."

## 26.2 Thermoelectric Properties and Their Measurement

### 26.2.1 Essential Requirements

Although a broad variety of techniques and devices for measurement of thermoelectric properties have been successfully applied, there are very few essential requirements which have to be fulfilled for high measurement quality in any of those methods. These are identified in the following.

#### 26.2.1.1 Seebeck Coefficient

When a thermoelectric material is subjected to a small and constant temperature difference ( $\Delta T$ ), a thermoelectric potential difference (thermo-voltage,  $\Delta V$ ) is produced. The Seebeck coefficient ( $\alpha$ ) of the material is defined as

$$\alpha = \Delta V / \Delta T \quad \text{as} \quad \Delta T \rightarrow 0$$

For accurate and reproducible measurement of Seebeck coefficient, the temperature difference  $\Delta T$  should be relatively small; the specimen homogeneous and spurious voltages of thermal origin should be eliminated. Furthermore it may also be necessary to take into account the absolute Seebeck coefficient of the contact material (solder, paste, etc.), especially if this is comparable to that of the material being measured. A simple and rapid method of measuring Seebeck coefficient is to apply a constant temperature gradient. However, when measuring at temperatures far from ambient, spurious thermally

induced voltages will become more significant in the measuring circuit. To minimize such effects it is recommended to measure the thermoelectric potential difference ( $\Delta V$ ) as a function of temperature difference ( $\Delta T$ ), the slope of the curve ( $d\Delta V/d\Delta T$ ) thus giving the overall Seebeck coefficient. The temperature gradient across the sample is varied whilst temperatures of all other parts of the apparatus are kept constant. To achieve this, measurements should be performed as quickly as possible. It is also important to minimize any effect of the thermal response time of the measuring system and therefore it is important that the temperature gradient is varied at a constant rate. Typically, the temperature difference should be as small as possible by definition, but practically a compromise has to be met in achieving sufficient measurement accuracy. Thus,  $\Delta T$  is usually of the order of 1 to 5 K.

Two essential requirements must be fulfilled for accurate Seebeck measurement. The first one is that the temperature of the contact junctions is exactly measured. This requires the temperature sensor to be located as close as possible to the junction (ideally at the junction as in the case of thermocouples acting both as potential leads for measuring the thermo-voltage). Zero heat flow along the measuring leads to the temperature sensor has to be adjusted in order not to disturb the temperature at the sensor. Inherently, if the sensor is not directly welded to the sample, there is a thermal resistance between sensor and sample. A second requirement applies in anisotropic media: a nondivergent temperature gradient (that is parallel heat flow) has to be maintained over the measuring region between the junctions of the potential leads.

### 26.2.1.2 Electrical Conductivity

Electrical current and voltage can be measured with very high precision. Thus, accuracy in determination of the electrical conductivity is merely limited by geometrical precision of sample shape, homogeneity, and contacting.

Accurate evaluation of electrical resistivity (or electrical conductivity) requires that contact resistances to the sample and thermoelectric effects due to sample heating are minimized and that sample boundaries and dimensions are accounted for. Many articles have been published on this topic (for example, see Valdes,<sup>7</sup> Runyan,<sup>8</sup> and others<sup>9,10</sup>) and as such, electrical resistivity measurements are usually the most accurate of all thermoelectric measurements.

The most common method of measuring resistivity is the four-probe method, since it virtually eliminates the influence of contact resistances. A linear array of equally spaced probe tips is placed on the surface of a disk-shaped specimen. A current is applied between the outer probe tips and using a very high impedance voltmeter, the potential across the inner probes is measured. From this sheet resistance measurement and details of the probe spacing, sample diameter and thickness, it is possible to obtain the electrical resistivity of the sample. To minimize thermoelectric effects, either a reversible dc current is employed or an ac current source, although the latter may introduce reactive effects at contact surfaces and stray coupling. Sources of error are typically due to inaccuracies in probe spacing, temperature gradients in the sample, distortion of current flux lines in small samples, and sample dimensions.

If a particular apparatus or procedure does not allow for exact consideration of geometrical effects, as may be the case in some high-temperature measurements, correction of the geometry factor can be achieved by an additional room temperature precision measurement in a suitable set-up allowing for high geometrical precision. Furthermore, stability of contacts at high temperature may be a cause for concern. This may require preceding and succeeding measurement in addition to obtaining the temperature-dependent data to ensure that no irreversible change has occurred at the contacts during the measuring series at high temperature.

### 26.2.1.3 Thermal Conductivity

Thermal conductivity has turned out to be the most difficult among thermoelectric measurements. Principal errors of direct methods are caused by thermal losses, thermal resistivity of interfaces, and available sample size. Flash methods offer an alternative although these do not provide the thermal conductivity itself but require further measurements: specific heat (associated considerable uncertainty

in a DSC measurement) and mass density. Thus, the overall error of the thermal conductivity easily accumulates up to 8%. However, the wide-spread availability and utilization of flash and DSC apparatus accompanied by established reference procedures and materials has resulted in its almost universal use.

In the flash technique, a disk-shaped specimen is exposed on one surface to an instantaneous burst of irradiant energy (usually a pulse laser) and the temperature history of the opposite surface recorded by means of either a thermocouple or infrared detector. Analysis of the temporal temperature change enables the thermal diffusivity to be obtained.

The popularity of the laser flash method has meant that consideration and analysis of errors in this method have been covered in depth. From experience, it is found that reproducibility of this method depends largely on the type of materials investigated, since these will influence signal to noise ratio of the detected temperature history and rate of change of temperature.

In addition to thermal diffusivity, specific heat may be measured either by means of the laser flash method (if a suitably calibrated laser source and detector are available) or using a separate system such as a differential scanning calorimeter (DSC; see for example, Refs. [11,12]). The principle of measuring  $c_p$  using DSC involves measuring the temperature difference between two identical crucibles as these are simultaneously heated at constant rate. Performing three identical temperature sweeps one crucible remains empty (a reference) whilst the other is either empty ("zero line"), contains a standard sapphire reference with known heat capacity, or finally contains the sample under test. Analysis of the three individual temperature sweeps together with specific heat data of the reference sample and sample weights enables the  $c_p$  value as a function of temperature to be obtained. Accuracy and reproducibility of  $c_p$  measurements depend critically upon several factors including placement of crucibles on the measuring stage, purge gas flow rates, small changes in surrounding temperature, contamination of crucibles, accurate weighing of samples, calibration of the DSC, and reproducibility of the zero line.<sup>13</sup> The search for synthesis of accuracy and simplicity has brought along the development of different constructional types (plate-type, cylinder-type) and measuring principles (heat flow calorimeter, temperature compensated calorimeter).

Emissivity-independent temperature and thermal properties measurements at the mm scale by the laser absorption radiation thermometry (LART) technique<sup>14</sup> could be useful for complementing TE measurements. Generally thermal radiation is a major problem when trying to control thermal conditions at elevated temperature. This makes thermal conductivity measurement difficult, especially under constraints imposed by simultaneous determination of the Seebeck coefficient and electrical conductivity. There is therefore considerable demand for reliable noncontacting and noninvasive thermometers. Conventional, passive, radiation thermometry is often subject to serious systematic errors resulting from poorly characterised emissivity or extraneous background radiation.

LART is a photothermal radiometry technique, combining radiation thermometry with infrared laser technology. It allows the temperature to be measured independently of target emissivity, target surface characteristics, optical path gaseous absorptions, laser beam intensity profile, and reflected back-ground radiation. The LART technique detects the small modulations in thermal radiances at two different wavelengths  $\lambda_1$  and  $\lambda_2$  due to photothermal heating of the target induced by chopped lasers at  $\lambda_1$  and  $\lambda_2$ , respectively. The ratio of these two modulated thermal radiances is a function of temperature and is independent of emissivity and other thermal properties. Work is in progress to extend the LART capability to measure thermal properties, for example, thermal diffusivity, thermal conductivity, and spectral emissivity as well as temperature.

## 26.2.2 Available Standards

### 26.2.2.1 Temperature Measurement

In general, all thermoelectric properties vary with temperature. Thus, precision in thermoelectric measurements requires precise temperature measurement. Standard wire thermocouples are most widely used here, followed by Pt resistance thermometers, Cernox thermometers, or semiconductor thermometers.<sup>15</sup>



Temperatures are reported in terms of the ITS-90.<sup>16</sup> The international temperature scale ITS-90 was established in 1990. It covers temperatures above 0.65 K and is based on a table of 16 fixed temperature points between the triple point of hydrogen (13.8 K) and melting point of copper (1357.77 K), and interpolating formulae for platinum resistive thermometers. Its main difference to its predecessors, IPTS-68 and EPT-76, is that thermocouples achieving not better than two tenths of a degree in absolute accuracy are not accounted any more as accurate enough to be the calibration reference for the standardized temperature scale as it has been before the Pt10Rh (S-type) thermocouple. Instead, platinum wire resistors, mainly Pt-100 (100  $\Omega$  at 0°C precision resistor) are employed, that reach at least one order of magnitude better accuracy and are not subject to problems such as inhomogeneity of the Seebeck coefficient in the current leads or aging (shift of sensitivity) as with thermocouples.

In thermoelectric laboratory practice, thermocouples are the most common tool for temperature measurement and are indispensable as RM for Seebeck measurement. Based on ITS-90 and IEC 584-1: 1995, calibration tables for several types of thermocouples (K, T, J, N, E, R, S, B) have been established by the national legal standards DIN EN 60584-1: 1996, BS EN 60584.1: 1996, ANSI/MC96.1, NF EN 60584.1: 1996, JISC 1602, and ASTM E230-96-1.<sup>17</sup> Besides the tables, the standards contain polynomials for interpolation for the usable temperature range. Whereas calibration values are available for all of the nonnoble metal thermocouples (K, T, J, N, E, R, S, B), merely Cu–CuNi (T-type) is recommended for reliable long-term application below room temperature. Part Two of these standards contains deviation limits of the tabulated values.

Reliable platinum resistive thermometers became available after nonintentional impurities and thermomechanical strain could be successfully suppressed. The legal standards DIN EN 60751: 1996 and IEC 751: 1983, respectively, define platinum measuring resistors. Pt-100 is standardized from –200°C up to 850°C. Above 600°C, because of its larger wire diameter, Pt-10 is more stable and thus preferable.

Manufacturers are recommending recalibration of thermocouples every 6 to 12 months by accredited laboratories. Those laboratories are accredited by national calibration services. Several European national services are joined in the Western European Calibration Cooperation (WECC) since 1990.

Apart from correct calibration, accurate temperature measurement requires good thermal coupling to the measuring object and the avoidance of heat flow along the measuring leads and self-heating (resistive thermometers).

### 26.2.2.2 Seebeck Coefficient

To date, no SRM for the Seebeck coefficient is available for typical thermoelectric materials. Seebeck measurement of thermoelectric materials is mostly a comparative method with a metallic thermocouple wire as a reference which can be traced to the above-mentioned standard thermocouples. To check the accuracy of a Seebeck measurement both a constant offset and errors proportional to the Seebeck coefficient of the sample have to be excluded. Thus, Seebeck calibration with reference materials should include a pure metal with low Seebeck coefficient (few  $\mu\text{V/K}$ ) like Pt, Pd, Cu, or others, as well as a reference material with higher Seebeck coefficient (preferentially several 10 to 100  $\mu\text{V/K}$ ). This could be CuNi (constantan) or NiCr (chromel) based on standardized thermocouples' calibration values. However, since these always represent a superposition of two materials, precise Seebeck data of a single material (preferentially Cu) have to be available. Precision Seebeck measurement on metals (Pb, Cu, Pt, and Ni) are provided and compared to previous data by Burkov.<sup>18</sup> High precision Pt–Pd thermocouples data<sup>19</sup> as well as special information covering the influence of chemical composition on the electrical properties of Pt<sup>20</sup> are reported.

Bulk Bi<sub>2</sub>Te<sub>3</sub> was chosen as a reference material below 300 K,<sup>21</sup> achieving good agreement to the data of Yim and Rosi.<sup>22</sup> IrSb<sub>3</sub> was used as a Seebeck reference material in the range 80 to 700 K.<sup>23</sup>

### 26.2.2.3 Electrical Conductivity

Although numerous high precision resistivity data are reported for metals, these values are much lower than the range of typical thermoelectric material. Pure Bi has been reported as a resistivity reference.<sup>23</sup> Clearly there is a need for provision of suitable RM among heavily doped semiconductors.

Increasingly, simultaneous methods become popular in thermoelectric measurement, mainly due to the reduced effort in preparation and time. Mostly, Seebeck and electrical conductivity measurements are combined for the low-temperature<sup>21</sup> and over elevated temperature range (80 to 700 K)<sup>23</sup> and also using universal apparatus for measurement on metals (Pb, Cu, Pt, and Ni) with high accuracy over a wide temperature range.<sup>18</sup> Simultaneous measurement on  $S$ ,  $\sigma$  has been extended to needle like samples,<sup>21</sup> and results are in good agreement with Physical Properties Measurement System (PPMS) measurement. Evidently, in these systems a double reference material (for both  $S$  and  $\sigma$ ) is required.

Apparatus providing a combination of electrical and thermal conductivity measurement, for example, the Combined ThermoElectric Measurements (CTEM) at DLR,<sup>24</sup> are less common. These again would require appropriate double RM. For example, graphite, stainless steel, electrolytic iron, and sintered tungsten, designated RM8424, SRM1460, RM8420, and SRM8422, respectively, have been issued by NIST as thermal conductivity and electrical resistivity standards.

### 26.2.2.4 Thermal Conductivity

Whereas thermoelectric standardization is still at an early stage of development, the situation is far more advanced for thermal and thermophysical measuring methods. Governmental authorities like NIST (U.S.A.), NPL (U.K.), PTB (Germany), and others provide materials science and thermal metrology expertise (advice and consultancy) to support on selection and testing of appropriate candidate RM and measurement approaches and its validation, providing traceability to national standards wherever possible. These may provide baseline thermal properties using national measurement standards or other high level apparatus for thermal conductivity, thermal diffusivity (using laser flash), emissivity (from sub ambient to 1700°C), heat capacity (using DSC), expansivity (push rod dilatometry), etc., including electrothermomechanical property measurements.

#### 26.2.2.4.1 Precision Thermal Conductivity Measurements of Metals

Precise absolute methods with external heater require large samples but under favorable conditions may reach accuracy up to 1%. Cu, Al, Fe, Mo and CrNi steel have been characterized up to 500°C. Very good coincidence of measurements on iron was obtained to recommended standard values.<sup>25</sup> A good survey on a multitude of apparatus of this type was given by Ref. [26], including methods of mathematical analysis of those measurements.

In a relative measurement, the thermal conductivity of the sample is obtained from the comparison to one or two RM. Usually those measurements are carried out between room temperature and 700°C, and occasionally at higher temperature.<sup>27</sup>

To avoid the problem of lateral heat losses, radial geometry is preferred. Samples are shaped as long and thick cylinders with a central hole for the heating. Thus, the sample volume may easily reach 200 cm<sup>3</sup>. Sometimes the samples are sliced and auxiliary heaters are applied to inhibit axial heat flow. A multitude of apparatus of this type has been developed, indicating accuracy values between 2 and 30%. A survey is given by Ref. [28] including a list of 25 metals and alloys characterized by radial methods.

Direct electrical heating methods use the Joule heat of the sample for measurement of the thermal conductivity. A heating current is conducted through a long sample and, along with voltage, current, and resistance, the radial temperature profile of the sample is recorded while axial heat losses are suppressed by a shroud. The basic idea was developed by Kohlrausch in 1900.<sup>29</sup> The method is quick and allows for avoiding a lot of technical problems at high temperature linked to joints between dissimilar materials as may occur with other measuring principles. As early as 1900 a fully operable setup was installed.<sup>30</sup> A rather complex method taking into account full temperature dependence of thermal conductivity, electrical resistivity, and thermal radiation, and being applicable up to 3000 K was developed by Taylor<sup>31</sup> where even pyrometry was involved to correct for the influence of the emissivity, and a sophisticated mathematical evaluation is required.

All of those precision methods share the feature of little suitability for thermoelectric materials since need large and mostly complicate to prepare samples which are required to be homogeneous. This is in



most cases unlikely to be fulfilled by thermoelectric semiconductors, but could be reached by constantan, recommending it as a possibly suitable candidate for a thermoelectric SRM.

#### **26.2.2.4.2 Low Thermal Conductivity Materials**

The thermal conductivity of reference solid materials was determined in Ref. [32], covering the interesting range for thermoelectric materials. Three RM, Pyrex 7740, Pyroceram 9606, and stainless steel AISI 304 L (also in Ref. [33]), with thermal conductivity values well in the range of thermoelectric materials have been studied by the transient hotwire technique in a temperature range from room temperature up to 570 K. The technique applied eliminates all remaining contact resistances, allowing for operating in an absolute way. The method is based on a full theoretical model applied to the exact geometry. At the 95% confidence level, the standard deviation of the thermal conductivity measurements obtained was 0.1% for Pyrex 7740, 0.4% for Pyroceram 9606, and 0.2% for stainless steel AISI 304 L, while the standard uncertainty of the technique is less than 1.5%.

As an alternative to the steady-state methods usually applied for thermoelectric materials,<sup>34</sup> dynamic measurement of thermal conductivity has been proposed as a comparably easy, fast, and accurate technique below room temperature. The technique allows to reduce the time of measurement for several hundred data points in a temperature range between 300 and 10 K during as short a duration as 90 min. It provides good precision and works with a simple experimental setup.<sup>35</sup> Reference measurement to the NIST SRM1415, Pyroceram 9606, gave good agreement. This was also found in comparing the measurements to steady-state methods. The measurements show an increasing with temperature deviation from standard values near room temperature with a typical overestimation of 15% at room temperature for samples of low thermal conductivity. This is similar to the behavior of the PPMS described below, likely linked to thermal radiation losses.

A steady-state method for measurement of thermal conductivity on thin fiber-shaped samples (few tenths of a mm in diameter) by a “parallel thermal conductance” method<sup>36</sup> has been developed. The demanding sample geometry requires high reproducibility of thermal contacts. As shown, the influence of contacts could be isolated by measurement on a thin Cu wire for computational separation in further measurements. A reference measurement to the thermal potentiometer method of Issi<sup>37</sup> was provided on a single carbon fibre.

#### **26.2.2.5 Thermal Diffusivity and Specific Heat**

Determination of thermal conductivity is more and more often accomplished by calculation from specific heat, thermal diffusivity, and mass density rather than by direct measurement of the thermal conductivity itself.

##### **26.2.2.5.1 Flash Methods for Determination of Thermal Properties at High Temperature**

Usually, steady-state heat flow methods are the standard way to determine thermal conductivity. This method works excellently at low temperatures, but at temperatures well above room temperature, it starts to fail, primarily due to radiation losses, extended time periods to reach thermal equilibrium, and uncertainties in the determination of temperature gradients at high temperatures.

To study thermal diffusivity, thermal conductivity, and specific heat in an accurate and reliable manner up to about 1700 K, flash methods provide better conditions. Well known commercial devices are for example, Netzsch LFA427<sup>38</sup> and LFA457.

Flash methods have the advantage of being fast while providing results with excellent accuracy and reproducibility. The outstanding feature of this technique, however, follows from the fact that for determination of thermal diffusivity absolute changes of the sample temperature need not be monitored; rather, a time-dependent measurement of the relative temperature increase is used which is much more accurate. Using flash methods for determination of specific heat involves measuring the absolute temperature rise of the specimen caused when a *known* amount of heat is deposited on its front surface in form of a light pulse. In order to receive reliable results and to get rid of a number of

problems usually associated with this type of measurement, multiple sample side-by-side testing (i.e., with one calibrated reference sample) greatly reduces problems and brings the overall errors within the same range as other calorimetric methods operating at high temperatures. The method exhibits a series of benefits:

- It requires only small samples.
- It is very fast; the actual measurement takes only a few seconds.
- The same instrument can be used for a large range of thermal diffusivities and thus for thermal conductivity from smallest to largest values.
- It can be used with proper precaution to measure other thermophysical properties (specific heat, thermal conductivity, etc.).
- It is capable of testing samples up to much higher temperatures than steady-state methods.

Laser flash methods combined to calorimetric data are a strong competitor to the traditional direct measurement of the thermal conductivity since there is a background of commercial device manufacturers which facilitates installation of characterization apparatus in a short time. Linked to the commercial background which also makes the methods more reliable, available, and comfortable, a lot of standardization activities and RM are related to laser flash and DSC measurement which finally enable the process to come close to the accuracy of direct methods.

#### **26.2.2.5.2 Standards for Determination of Specific Heat by Differential Scanning Calorimetry**

The long history and wide-spread application and commercialization of measurement of specific heat by differential scanning calorimetry (DSC) have brought along a wide spectrum of RM and detailed experience on calibration methodology. DSC method and apparatus are, for example, described in Ref. [39]. A survey on DSC calibration is given in Ref. [40]. Two international standards on DSC measurements are fixed in Refs. [41–43].

Reference data on the specific heat of alumina have been provided from  $-50$  to  $600^{\circ}\text{C}$  and from  $80$  to  $1600^{\circ}\text{C}$ , and for POCO AXM 5Q graphite between  $-100$  and  $1300^{\circ}\text{C}$ <sup>44</sup> under inert atmosphere. These show high reproducibility, a high degree of coincidence between a low-temperature and high-temperature measurement, and accordance to literature data<sup>45</sup> within 2.5% over the whole temperature range. Further reference values for pure monocrystalline alumina (synthetic sapphire) are given in Ref. [46].

DSC calibration to higher temperatures has been described<sup>47</sup> using Ti up to  $800^{\circ}\text{C}$  and Ni to  $1600^{\circ}\text{C}$ . The best measuring performance is achieved with plate-like samples rather than with powders or irregular shaped samples. For precise high-temperature measurement, performance of cylindrical calorimetric systems is superior to common plate-shape measuring systems. Errors in this study were up to 2 to 5%. The specific heat of Pyroceram 9606 has been measured between  $50$  and  $1000^{\circ}\text{C}$ , with deviations from literature values<sup>48</sup> generally less than  $\pm 2\%$ .

Generally, the more reference substances are involved in DSC calibration, the higher is the accuracy achieved. In daily laboratory practice, about four different samples distributed over the temperature range are recommended.<sup>49</sup> The possibility of measurements under very pure atmospheres as, for example, in the NETZSCH DSC 404 C Pegasus developed for tests between  $-120$  and  $1650^{\circ}\text{C}$ , allows measurements on materials sensitive to oxidation.

A most comprehensive compilation of calorimetric RM is found in Ref. [5] as the results of the ICTAC working group Thermochemistry 1997/1998 based on previous summaries.<sup>50,51</sup> The publication lists detailed reference data on about 15 RM, most of them in the near room temperature region, but also over a wide temperature range, such as alumina, Pt, Cu, Mo. Recent original works have been dedicated to  $\alpha$ -aluminum oxide<sup>52</sup> and Cu.<sup>53</sup> The suitability of the enthalpy of fusion of metals for standards at moderate to high temperatures is discussed in Ref. [54].

The Dutch Society for Thermal Analysis (TAWN) has initiated an exemplary interlaboratory test in 1997 named “TAWN tests for measuring resolution and sensitivity of DSCs” involving 47 laboratories which comprised a standardized series of experiments to quantitatively evaluate performance of DSC

devices from various manufacturers.<sup>55</sup> Focus was laid on easy procedure and evaluation of the test, suitable to any usual heat flow calorimeter. Remarkably, the results obtained in different devices of the same type and manufacturer differed considerably, especially with respect to the signal-to-noise ratio. This was interpreted as an effect of contamination of the measuring cells, and a wide scatter of sensitivity of systems of equal type.

#### **26.2.2.5.3 Standards for Laser Flash Measurement of Thermal Diffusivity**

An austenitic steel certified as NIST SRM1460 was proposed and characterized by Henderson et al. as a thermal diffusivity standard for the LFA.<sup>56</sup> The work provides a short survey on available standards for the LFA. Despite LFA being so broadly accepted, almost no reliable reference standards exist for the laser flash method although there are a lot of thermal conductivity standards available.

Work has been done intending to establish POCO AXM-5Q1 graphite as a thermal diffusivity standard but the consistency of available LFA measurements is somewhat in question.<sup>45</sup> Glass ceramics, such as Pyroceram 9606, have the disadvantage of being translucent, so these have to be coated on both sides for measurement but suitable coatings tend to diffuse into the sample upon heating. So specific heat and thermal diffusivity of several SRM1460 samples were repeatedly measured and an anomaly of its temperature dependence was observed near 600°C.<sup>56</sup> From SRM1460 thermal conductivity reference data and measured specific heat and thermal expansion data, the thermal diffusivity was calculated taking into account the temperature dependence of the mass density. The result was compared to the measured values of thermal diffusivity. Both the measured and calculated values could be obtained with an uncertainty of about 5% and coincided within 3% between 50 and 850°C.

Furthermore, laser flash reference measurements were taken on a glassy carbon.<sup>57</sup>

#### **26.2.2.5.4 Novel Transient Methods for Determination of Thermal Properties**

Recently, movement towards extension of both the laser flash and DSC principles for simultaneous determination of thermal conductivity, thermal diffusivity, and specific heat can be noted. Inspired by computer-assisted temperature control and evaluation, and realistic transient thermal modeling of complicated geometries, the superposition of the phenomena covered by both LFA and DSC methods can be analytically decoupled. Accuracy is approximating that of traditional methods of thermal properties measurement but sample size and geometry are much smaller and easier. Thus, these techniques seem most adequate for characterization of thermoelectric materials since they comply with mostly small available amounts of sample material.

A laser flash apparatus for simultaneous measurements of thermal diffusivity and specific heat of solids has been reported upon, thus achieving a differential laser flash calorimetric method.<sup>58</sup> Thermal diffusivity, specific heat, and thermal conductivity of glassy carbon (studied as a candidate of SRMs of thermal diffusivity by the National Research Laboratory of Metrology [NRLM], Japan) and molybdenum (SRM781 of NIST) were measured in the temperature range from 300 to 1100 K. The apparatus is capable of simultaneously measuring thermal diffusivity and specific heat with small uncertainty and obtaining thermal conductivity by a single shot of laser pulse. Two specimens, measured and reference material, are required. As a crux, equal emissivity of the surface for both specimens is essentially important for specific heat measurements. For both Mo specimens with 10 and 5 mm of diameter, the results showed agreement within  $\pm 2\%$  for thermal diffusivity, within  $\pm 1\%$  for specific heat and within  $\pm 3\%$  for thermal conductivity, respectively. The results of the simultaneous measurement of two specimens of glassy carbon showed good agreement within 1%.

Original measurement of thermal conductivity in a DSC at an accuracy of 10% for thermally low conducting materials of 0.1 to 2 W/(m K) has been reported elsewhere.<sup>59</sup> A similar publication<sup>60</sup> claims a much wider range of thermal conductivity even (0.1 to 500 W/(m K)) where modern AC calorimetry can be applied. However, standard materials have not been measured yet for check. This method seems to open options for much less cost-intensive measurement than by laser flash and gives a rough estimate of thermal properties of a small sample.

#### 26.2.2.6 Figure-of-Merit

As outlined above, there are two SRMs available for both electrical and thermal conductivity which, although at the margin of the resolution, are applicable as RM for thermoelectric characterization apparatus. Furthermore, standardized thermocouple tables and precision measurement on pure metals provide reliable Seebeck data. Currently there are a very small number of pure metals (Cu, Pt) with comprehensive data on all thermoelectric quantities ( $S$ ,  $\sigma$ ,  $\kappa$ ) sufficient to precisely calculate the figure-of-merit  $Z$ . However, the obtained values are out of the range of practical laboratory needs. A better choice, since their  $Z$  values are lying within one order of magnitude with good thermoelectric materials, would be thermocouple alloys like constantan and chromel. These are advantageous because of their industrial background of production methods and facilities, and commercial availability. Mainly the reproducibility and stability of thermal properties have to be studied here. Clearly, there is a requirement for certified RM suitable for the field of thermoelectric semiconductor research.

The proposal to choose a thermoelectric semiconductor itself as a standard faces a number of problems such as common availability, chemical purity, reproducibility of preparation, homogeneity, scale of batches, long-term stability or volatility of components, poor mechanical properties, contacting issues, and limitation to a narrow temperature range. Probably, identifying any thermoelectric material as a reference would mean a compromise in any case.

Such a desired  $Z$  standard would unify the capability to act as a reference material for each of the measurements of  $S$ ,  $\sigma$ ,  $\kappa$ , as well as for direct measurement of  $Z$  as in the Harman method. Simultaneous methods like the CTEM may play an important role in the course of establishing those standards since they allow measurement of all quantities for the same sample.

### 26.3 Strategies toward Standardization

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#### 26.3.1 Calibration of Components

Thermoelectric measurement facilities are complex apparatus involving several functional units measuring auxiliary quantities like temperature, voltage, current, and magnetic field. These data will be involved in the overall accuracy of the thermoelectric measurement. General guidance on improving measurement accuracy and reproducibility of those common quantities is provided by national institutions for standardization. Temperature measurement has to be standardized using suitably calibrated temperature sensors (see above). Voltage and current measurements have to be calibrated against reference sources. Calibration services are offered by many suppliers. Magnetic measurements such as Hall and Nernst effect will require appropriate calibration of magnetic field sources.

#### 26.3.2 Provision of Thermoelectric Materials Standards

For many years, the requirement for standardizing thermoelectric transport properties measurements existed among the thermoelectric community. Although there is today a large number of laboratories performing thermoelectric evaluation by mostly in-house built measurement facilities, each laboratory is itself responsible for checking the reproducibility and reliability of the measured data. This requires the usage of RM, i.e., samples provided of well-defined quality by an authorized supplier with certified characteristics which meet fixed accuracy limits. As yet, there remain very few certified RM available for standardizing measured quantities used in thermoelectric semiconductor material development. Of those materials certified as RM by suppliers such as NIST, the transport properties are generally within different ranges of magnitude than are required.

Such standards are available to date only for electrical and thermal conductivity but are completely missing for figure-of-merit and performance of thermoelectric devices (Peltier and thermogenerator modules; COP and efficiency). It is a main practical target of thermoelectric standardization to identify suitable reference samples, to provide reproducible fabrication processes, and reliable data on the

thermoelectric properties. Another target is to define measuring sample geometry, sample holders, measuring conditions, and procedures which guarantee accurate results.

As standards on thermoelectric materials preparation and quality are not available, definition of these would be a first step towards reference thermoelectric materials. To enable fabrication of RM as a laboratory scale production, suitable standard materials for thermoelectrics have to be identified first. These have to be synthesized and manufactured in a sufficiently reproducible manner and in large enough batches of high homogeneity. Otherwise, significantly different values would be obtained from several parts of one batch or ingot. Accordingly, fabrication methods have to be identified and qualified.

Lyon<sup>61</sup> presented a proposal on validation of thermoelectric measurement to the International Thermoelectric Society in 1994 and suggested that perhaps samples of well characterized bismuth telluride materials could be made available to the thermoelectric community at a cost. The proposal listed a multitude of technical problems which are related to the provision of a suitable reference material. It was agreed that no preparation process of thermoelectric materials was available at that time which could ensure sufficient homogeneity over an ingot of high performance thermoelectric material large enough to prepare sufficiently many individual reference samples from it. A suitable program for certifying the materials would be required, although Lyon indicates that individual characterizations of samples supplied would be too costly. Thus, a process was suggested which involves concerted standardization action of numerous laboratories based on real inhomogeneous materials (i.e., nonidentical reference samples) and feeding back measurement results to the supplier. The measuring results would be correlated with the location in the original ingot, thus establishing accurate data on the reference material during the interlaboratory exchange itself. Suitable modeling would be adopted by the supplier to convert surface resistivity measurements from intermediate calibration slices cut from the crystal rod into the primary thermoelectric transport properties, these being “mapped” to customers’ samples.

Such a process could lead to standardization of thermoelectric measurements; however, the choice of a suitable material is still questionable. Moreover, involvement of a theoretical model would add a factor of uncertainty. The exact quantitative validity of the model has to be ensured first covering the whole variation range of the composition of the RM. The logistic effort would be high. The success of the whole action would widely depend on reliable simultaneous action of the participants.

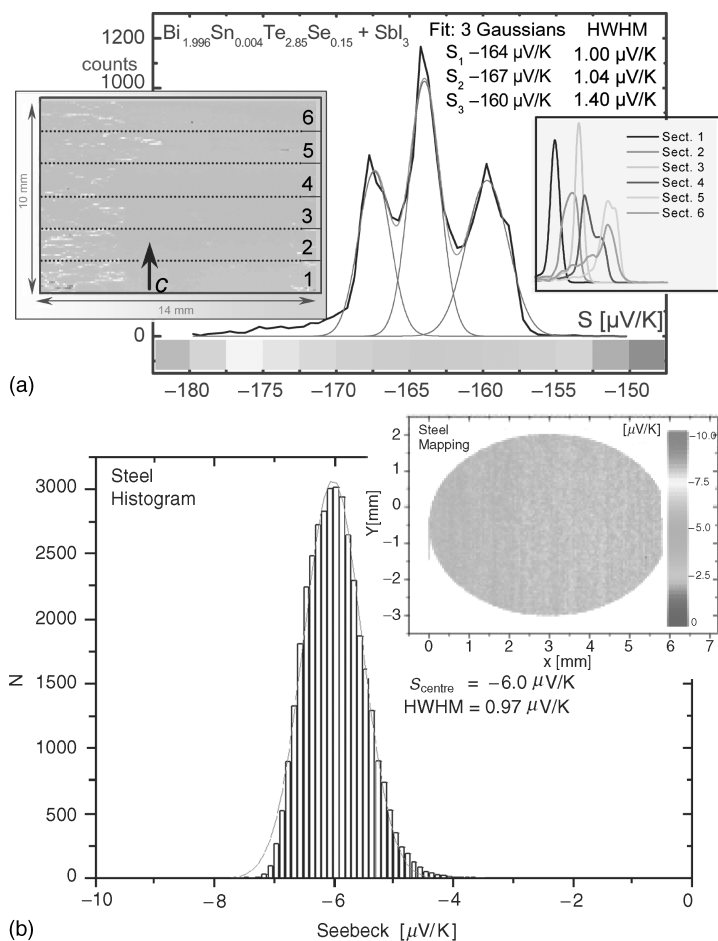
Advanced methods of material preparation yielding sufficiently homogeneous materials with high reproducibility may make such a complex procedure a nonstarter. An automated technique for characterization of the homogeneity of thermoelectric materials may play a key role in that process. A scanning Seebeck microprobe (SMP) has been developed<sup>62</sup> which allows for automatic mapping of the Seebeck coefficient in an arbitrary two-dimensional pattern at a flat surface of a thermoelectric material. The technique has been successfully applied to a wide spectrum of currently investigated thermoelectric materials, and agreement of mean values of those mappings to conventionally measured integral values of the Seebeck coefficient has been demonstrated. The reproducibility of the SMP measurement has been checked by multipoint measurements on highly homogeneous samples ( $\text{Bi}_2\text{Te}_3$ , stainless steel) where a deviation (half peak width at half maximum [HWHM]) of about  $1 \mu\text{V/K}$  was achieved.

If linked to a semi-industrial method of material production which should be able to produce about 1 kg of material in large blocks per day, the SMP technique would allow for selecting homogeneous regions from those blocks big enough to cut from them many reference samples of mm to cm size as is common in laboratory practice.

Fabrication techniques like gas atomizing for powder production, ball milling, cold and hot pressing of powders, extrusion, and furthermore quenching but also crystal growth (Czochralski, zone melting), and others seem suitable to fulfill these requirements. Large compacts of 80 mm in diameter and 15 mm in thickness of doped iron disilicide have been prepared at DLR by hot uniaxial pressing and mapped by SMP. Control of the Czochralski process to grow large-size  $\text{Bi}_2\text{Te}_3$  crystals<sup>63</sup> has shown tremendous progress during recent years. The method is capable to produce  $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$  crystals of up to 1 kg in weight. Within 8 h, ingots of 40 to 50 mm in diameter and 80 to 120 mm in length can be grown which contain large regions with extremely homogeneous thermoelectric properties.<sup>64</sup>

In Figure 26.1a, the homogeneity of a crystal over a size of 15 mm has been shown, where the variation of the Seebeck coefficient is in the order of magnitude of the reproducibility of the SMP method (about  $1 \mu\text{V/K}$ ). Seebeck mappings can be recorded by SMP on cutting faces of the ingot during the fabrication of reference samples. However, these materials are single crystalline, and thus have to be handled with care.

Suitable RM have to be mechanically, thermally, chemically, and functionally stable, readily available, desirably nonpoisonous, and have to allow easy mechanical shaping without mechanical damage or modification (microcracks) of the sample. Any treatment during preparation of reference samples has to avoid too high a temperature (which may change the microstructure) and aggressive media for etching or polishing, in particular in case of porous or layered sample materials. For careful control of powder processing, environmental chambers have to be used facilitating material handling under inert conditions. Sample cutting and polishing procedures have to conform to the material's specifications (vibration load, temperature range). The diffusion of doping species has to be widely avoided during



**FIGURE 26.1** Seebeck mappings and histograms of SMP measurements on  $\text{Bi}_2\text{Te}_3$  and stainless steel HWHM values of  $1 \mu\text{V/K}$  have been obtained by the method. (a) Map of a  $10 \times 14 \text{ mm}^2$  area of a homogeneous  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3\text{Sn}$  crystal grown by the Czochralski method. The histogram for the entire map is fitted by three Gaussians. Each of the peaks can be locally assigned to a section of the crystal (numbered in the left inset). The right inset shows partial histograms for each of the sections. (b) SMP analysis of an elliptic area ( $5 \times 6 \text{ mm}^2$ ) of a steel sample.



preparation. Adequate procedures for contacting of such standard materials have to be developed to avoid change of the properties due to mistreatment during the necessary handling in preparation for a reference measurement. Temperature limits as well as heating or cooling rate limits have to be indicated which must not be exceeded during any phase of the reference sample's life.

Suitable RM should cover a wide temperature range, exhibit high Seebeck values (50 to 500  $\mu\text{V/K}$ ), high electrical conductivity, low to medium thermal conductivity (1 to 20  $\text{W/(m K)}$ ), and low Hall coefficient. Several standard materials have to be defined covering both polarities (p- and n-type) and temperature ranges.

For stability reasons, a thermoelectric standard material should contain only a few chemical components. Possibly a binary compound with one doping element in a concentration which is well detectable by elemental analysis is appropriate. For example,  $\text{Bi}_2\text{Te}_3$ , doped  $\text{CoSb}_3$ , Mn- or Co-doped  $\text{FeSi}_2$ , doped  $\text{Si}_{1-x}\text{Ge}_x$  (which has already been prepared by ball milling and hot pressing) should be considered, each in its best temperature range.

### 26.3.3 Intra- and Interlaboratory Testing

The general lack of affordable commercial equipment to perform accurate thermoelectric measurements means that such facilities are more often than not designed and constructed in-house, although the principles of measurement are well established. The individual design of such facilities will therefore result in differences arising, not only with the temperature range of operation but in the geometry of the samples required, the accuracy, and the reproducibility of measurements.

In order to standardize and compare measurements between institutions on the same material, it is first necessary to identify these differences and then reach a compromise in sample size and geometry. Where the geometrical range of sample sizes of different apparatus is incompatible, identical properties of differently shaped reference samples have to be ensured (for example, by evidence of homogeneity by means of scanning methods; see above).

Round-robin tests will also require agreement on measuring conditions (maximum temperature range, atmospheric conditions, maximum mechanical loads to the samples, handling, and storage precaution) and will eventually require timely coordination. For thermoelectric materials, round-robin testing should cover thermophysical, electrical, and thermoelectric quantities: Seebeck coefficient  $S$ , electrical conductivity  $\sigma$ , thermal conductivity  $\kappa$  at minimum, but furthermore desirably thermal diffusivity, specific heat, and the thermoelectric figure-of-merit. Here, a comparison between calculated values of the figure-of-merit (from  $S$ ,  $\sigma$ ,  $\kappa$ ) to directly measured values (Harman method) might yield valuable conclusions on measurement accuracy and may reveal systematic differences in the redundant measurement principles, as are the role of thermal contact resistance and possibly the role of interfaces in the Harman measurement. Similarly, systematic measurement errors might be separated by comparison of thermal conductivity (directly measured by an absolute or comparative method) to its calculated values from thermal diffusivity and specific heat. Further quantities involved in round-robin actions may be the Hall coefficient, but also parameters of device performance (COP of TE refrigeration and energy conversion efficiency). TE modules of established commercial producers are suitable as testing objects here. Doubtless, inevitable scattering of individual device properties makes the procedure more complicated. Direct comparison is allowed for measurement on the same piece only. Thus, samples have to be circulated among the laboratories instead of parallel actions.

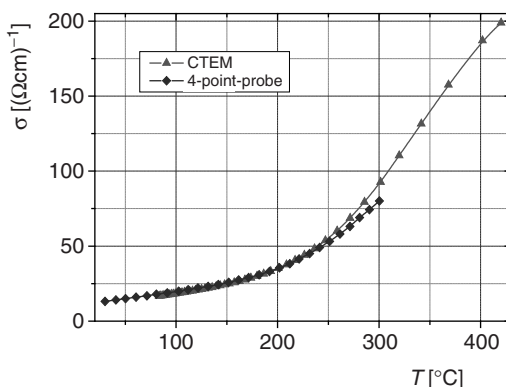
Round-robin tests need be as easy as possible to involve many laboratories. Comparison of the results will help to identify reasons for systematic deviation and improve the participants' facilities and procedures to reduce measurement uncertainty. It would be desirable also to involve a range of available commercial equipment (PPMS, LFA). For performance evaluation of DSC, round-robin activities have been taken place in the past in a singular action (TAWN tests)<sup>55</sup> which provides a benchmark also for today's device developers.

### 26.3.3.1 Intralaboratory Testing: Comparison of Alternate Principles and Overlapping Temperature Ranges—An Example

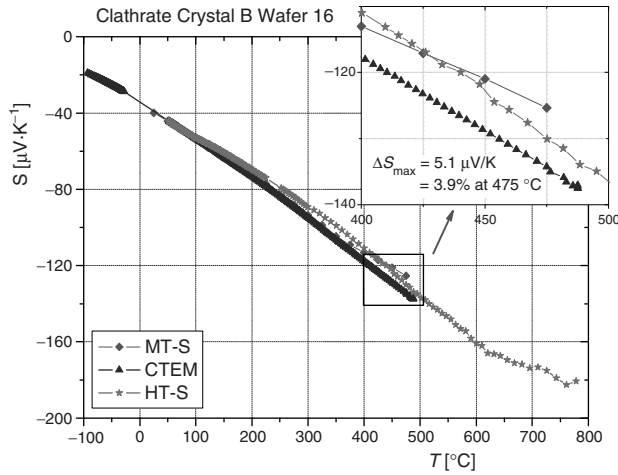
The German Aerospace Center (DLR) in Köln is running four facilities for measurement of the electrical conductivity, designed for evaluation under different conditions (temperature range, atmosphere or vacuum, sample geometry), among them CTEM (80 to 750 K), four-point desktop facility (sample on a heater plate under laboratory atmosphere; 300 to 600 K), Hall facility (vacuum, 12 to 330 K), and high-temperature facility (vacuum, 400 to 1100 K). The Hall facility and CTEM are overlapping within 80 to 330 K, the CTEM and high-temperature facility overlap within 400 to 800 K, and three out of all the apparatus overlap in 300 to 330 K and 400 to 600 K, respectively. The overlapping regions allow for intralaboratory comparison to estimate accuracy and eventually reveal sources of systematic errors. Figure 26.2 shows the comparison of the CTEM and the four-point inline apparatus. Very good agreement is found over most of the overlapping temperature range whereas an increasing deviation appears at the upper end of the temperature range of the four-point probe (above 240°C). A difference between the nominal sample temperature measured at the bottom side of the sample (close to the heater plate) and the real temperature at the location of the conductivity measurement at the surface where air convection cools the sample was found as a reason. This error is becoming significant for samples with strong temperature dependence, low thermal conductivity, and several mm thickness. For samples thinner than 1 mm, the deviation remains negligible.

Three apparatus for measurement of Seebeck coefficient have been compared at DLR in an intralaboratory test. In the CTEM (80 to 750 K), the prismatic bulk sample is connected via its base faces to Cr-plated Cu blocks which contain gradient heaters. Temperature difference and thermo-voltage are measured between these blocks. Thus, the soldered connection between blocks and sample represent a possible source of systematic error. Different sample geometry is used in the medium temperature Seebeck measurement (MT-S; 80 to 800 K) where thermocouples are led through central holes in small gradient heaters and both the heaters and thermocouples are separately mechanically pressed directly against the plate-like sample. Measurement in both CTEM and MT-S is taken in steady-state. A simple high-temperature Seebeck apparatus (HT-S) doing without gradient heaters and stabilization provides nonsymmetric thermal conditions to a plate-like sample and simply records voltages and temperatures during passive cooling down of the measuring head. Figure 26.3 shows measured data on a clathrate sample by all three apparatus in an overlapping temperature range (50 to 475°C). The largest deviation between the apparatus amounts to  $\pm 5.1 \mu\text{V/K}$  at 475°C according to a maximum deviation from the mean value of 3.9%.

Two different techniques of thermal conductivity measurement are performed at DLR: calculation from thermal diffusivity (LFA), specific heat (DSC), and mass density as mentioned above, and a

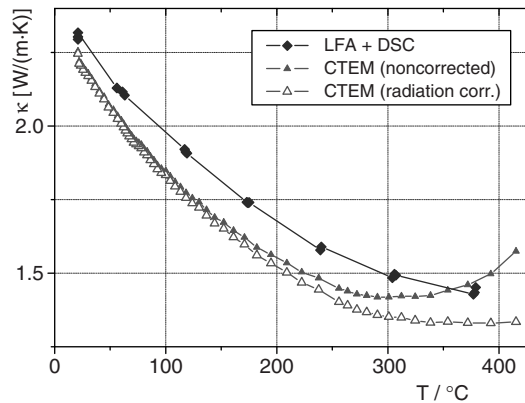


**FIGURE 26.2** Comparison of the electrical conductivity measured on a skutterudite sample (#1312; 2.1 mm thick) in the CTEM and the 4-point inline facility on atmosphere.



**FIGURE 26.3** Comparison of the Seebeck coefficient measured on a clathrate sample (NanoThermEl B#16) in three different apparatus including CTEM and high-temperature facility. The inset shows the temperature range of largest deviation.

transient method comprised of the CTEM where the time constant of the relaxation of the temperature difference between the Cu blocks via the sample as a thermal resistance is recorded. The results are corrected for the influence of the heat capacity of the sample and for thermal bypasses due to radiation coupling to the container walls. An unknown systematic reduction of the measured value occurs due to the serial connection of the sample to the parasitic thermal resistance of the interfaces to the Cu blocks which depends on both the sample material and contacting method. The comparison of both methods (Figure 26.4) reveals deviations of about 10% with the CTEM providing smaller values, probably due to parasitic thermal resistance of the interfaces. A minimum sample length of 3 to 5 mm is necessary to keep this error low. Variation of length may help to separate and eliminate the error. Above 300 K, CTEM provides too large thermal conductivity values unless these are corrected for radiation bypasses. Comparison to the LFA plus DSC measurement may help to verify the weighting of the radiation correction, which becomes critical at 300 to 400 K and above. Compact sample size (10 mm or more in diameter is recommendable) reduces the influence of this source of error.



**FIGURE 26.4** Comparison of the thermal conductivity measured on a skutterudite sample (NanoThermEl #1369) via laser flash method and CTEM. The influence of the radiation correction on CTEM thermal conductivity values is demonstrated.

### 26.3.3.2 Interlaboratory Testing—Current Situation and Next Steps

Facing a lack of suitable highly doped semiconductor SRMs or CRMs, interlaboratory comparison has initially to rely on suitable “off-the-shelf” RM. Using existing SRM with transport properties as close as possible to thermoelectric materials, a comparison of measurement accuracy and reproducibility near room temperature is feasible. Limitations of temperature range, measurement accuracy, and reproducibility for existing standard samples have to be assessed and thus a suitable list of recommended materials identified. Full reports on calibration, accuracy, and reproducibility of facilities can be established using SRMs identified above. It is essential that verification of possible changes in samples due to high temperature, aging, or other reasons is done by means of repeating measurements again after external measurement (for example, after the end of an round-robin cycle) at the supplying application laboratory.

To facilitate smooth sample exchange in interlaboratory activities, recommendations on preferable sample shape and size, or sample holders allowing for variable sample size should be agreed prior to standardization actions. A tablet shape which may be easily cut from cylindrical ingots or directly obtained by pressing seems favorite for routine thermoelectric characterization. Agreement should also be reached on contacting techniques.

### 26.3.3.3 Round-Robin Testing in the EU Project NanoThermEl

In 2001 to 2004, the European Commission funded the Specifically Targeted Research Project NanoThermEl, which combined the expertise of several leading research centers from across Europe in developing improved thermoelectric materials with reduced thermal conductivity, based on nanosized particles.<sup>65</sup> As the need for ensuring accurate and consistent experimental data is crucial for the success of any materials development programme, an essential requirement in this programme was the thermoelectric characterization of new samples including measurements of Seebeck coefficient, electrical conductivity, thermal conductivity, and the dimensionless figure-of-merit  $ZT$  over a wide temperature range.

A comprehensive survey on thermoelectric standardization activities in NanoThermEl was given by Williams.<sup>66</sup> A considerable number of samples had to be evaluated throughout the project, this work being divided between two leading European thermoelectric characterization laboratories, the NEDO Center at University of Cardiff, U.K. and the German Aerospace Center (DLR), Germany. The use of different measurement techniques, sample geometrical requirements, and equipment, however, meant that some form of measurement standardization was necessary between partners. This section describes how this was achieved by defining suitable standardization and round-robin tests. Such tests are expected to encourage further such standardization to be carried out between thermoelectric materials research laboratories, thus increasing confidence and the traceability of published data.

A series of interlaboratory tests were necessary to ensure meaningful and comparative data between NEDO, Cardiff and DLR. Both partners were responsible in NanoThermEl for evaluating the properties of improved thermoelectric materials. A preliminary comparison of thermoelectric transport measurements was also made against a commercial PPMS at the University of Århus, Denmark. Where possible, standard certified RM obtained from NIST was used. In other cases, suitable metal alloys and thermoelectric materials produced in-house were employed.

In this work, we include both PT and round-robin testing through an ILC. Both Cardiff (NEDO) and DLR have extensive facilities to evaluate the parameters which constitute the figure-of-merit of a thermoelectric material individually, all as a function of temperature.

#### 26.3.3.3.1 Cardiff Facilities

Electrical conductivity measurements are made at room temperature using a commercial four-probe apparatus (Jandel Scientific). For low-temperature measurement of Seebeck coefficient and electrical resistivity,<sup>67</sup> a closed-loop He cryostat is employed. For high-temperature simultaneous measurement of both Seebeck coefficient and electrical resistivity, suitable apparatus has been designed and constructed which applies both techniques described above and employs disc-shaped specimens. Thermal diffusivity is measured using the popular laser flash method<sup>68</sup> and uses a custom-built apparatus<sup>69</sup> where a vacuum furnace enables samples to be heated to 900 K. A disc-shaped sample (4 to 8 mm diameter) can be

measured with typical thickness ranging from 0.2 to 2 mm. Specific heat measurements require smaller samples, typically 50 to 100 mg in weight and 3 to 6 mm in diameter. A DSC (Netzsch DSC200 PC) system is employed and covers the temperature range  $-100$  to  $600^{\circ}\text{C}$ . The specific heat  $c_p$  is obtained using the ratio method. Sample density is obtained by weighing to  $10\ \mu\text{g}$  with a microbalance. Sample dimensions are measured using a standard micrometer to within  $0.005\ \text{mm}$ .

#### 26.3.3.3.2 DLR Facilities

Room temperature Seebeck coefficient measurements and locally resolving homogeneity testing are performed using a scanning microprobe (SMP) apparatus. Based on the hot-probe technique known for a longtime the apparatus is capable to measure the Seebeck coefficient by means of a heated probe tip and a heatsink platform. Two loops of copper and constantan wires, respectively, are closed when the probe is touching the sample. From the voltages of both loops which are measured using microvoltmeters, the Seebeck coefficient of the sample is calculated. Simultaneously, the temperature of the probe and the sample are recorded, as well as the vertical position of the probe tip. Both the probe leveling ( $z$  axis) and  $x$ - $y$  sample platform are controlled automatically.

The CTEM facility is capable of measuring the Seebeck coefficient between  $-150$  and  $500^{\circ}\text{C}$  simultaneously to other thermoelectric parameters. Its principle is described in Ref. [70].

An additional facility provides Seebeck measurement to  $800\ \text{K}$  and permits quick and easier sample exchange. For this system, however, longer plate-shaped samples are required ( $>8\ \text{mm}$  in length). At both ends, the sample is pressed against heater blocks by ceramic rods and high temperature springs. K-type thermocouples guided through channels in the heater blocks to the sample surface record temperature difference and mean sample temperature. A computer system and data logger permits full automation of the measurement process. The thermo-voltage is recorded for a variety of temperature gradients and the Seebeck coefficient is obtained from a least squares fit to separate  $d\Delta V/d\Delta T$ . A reproducibility of 3% was achieved with this system.

For room temperature electrical conductivity measurements, DLR employs both a conventional four-probe apparatus and the CTEM. The four-probe apparatus differs from that at Cardiff in that an ac sample current is employed and the resultant voltage is resolved using a lock-in amplifier. The CTEM apparatus is also capable of measuring thermal conductivity from the timely decay of the measured Seebeck voltage. The time constant of the decay is determined and a correction factor applied which accounts for the heat capacity of the sample holder and heat losses from the sample.<sup>71</sup> Also, DLR uses the laser flash method of measuring thermal diffusivity together with DSC  $c_p$  measurements for reaching higher temperatures in determining thermal conductivity. The commercial laser flash system (Netzsch LFA427) is capable of measuring from room temperature to  $1450^{\circ}\text{C}$ ,<sup>38</sup> as is the commercial Netzsch DSC404 system employed at DLR. The figure-of-merit,  $ZT$ , can also be measured directly from the CTEM apparatus using the Harman method.<sup>72</sup>

#### 26.3.3.3.3 PPMS at University of Århus

A comparison of measurements was also made against a commercial PPMS from Quantum Design.<sup>73</sup> The PPMS is primarily designed for low-temperature measurements ( $1.8$  to  $400\ \text{K}$ ) and provides automated measurement of the temperature dependence of thermoelectric parameters including Seebeck coefficient, electrical resistivity, thermal conductivity, thermal diffusivity, specific heat, and  $ZT$ .

Electrical resistivity measurements by PPMS are made using the standard ac four-probe method. Seebeck coefficient and thermal conductivity are measured simultaneously on a bar-shaped sample. The temperature difference used to measure the Seebeck coefficient varied from  $2.8\ \text{K}$  at the lowest measurement temperature to  $3.7\ \text{K}$  at  $400\ \text{K}$ . The measurement of thermal conductivity uses a nonsteady-state technique based on analysis of the time constants for heating and cooling the sample.

#### 26.3.3.3.4 Samples for NanoThermEl Interlaboratory Tests

For electrical resistivity and thermal standardization, a CRM from NIST (austenitic stainless steel SRM 1460) was chosen. This material has been certified by NIST in its document 260-90 special publication.<sup>74</sup> According to NIST, the high-temperature electrical resistivity data are believed to be accurate to about

1 or 2%, whilst thermal conductivity data accuracy varies from about 1 to 5%, except where noted. Thermal diffusivity and specific heat data on this SRM have been measured independently by Henderson et al.,<sup>56</sup> and this source was used as a comparison.

Since no standard reference material was available for Seebeck measurements calibration, a sample of chemically defined constantan alloy (block shape) was initially chosen for this purpose. Standard thermocouple tables were used to derive certified temperature vs. Seebeck voltage data for this material. A sample of palladium foil (Alfa Aesar, 99.9% purity [metal basis], 25  $\mu\text{m}$  thick) was also used for Seebeck standardization as this material was known to have reproducible and stable electrical properties; data for this material were also obtained from the literature. For round-robin testing, hot-pressed skutterudite samples of  $\text{CoSb}_3$  doped with Te and Ni<sup>75</sup> were chosen since these materials were being evaluated as part of the current materials development programme.

All measurements were made on the same samples where possible, and to this end a suitable sample geometry and size was chosen to be compatible with both laboratories. Eight-millimeter disk-shaped specimens were used, except when a smaller sample was required (such as in heat capacity measurements) and this was cut from the same disks using an ultrasonic cutting tool.

### 26.3.3.3.5 Results

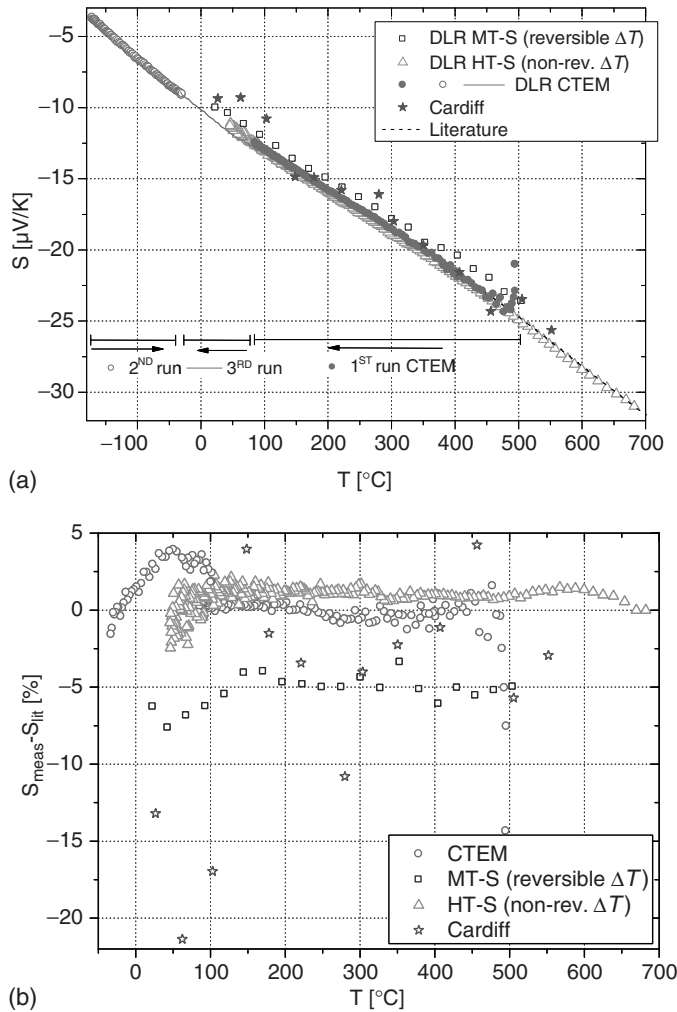
A comparison of Seebeck coefficient measurements over the temperature range 300 to 900 K for the Pd foil sample between Cardiff and DLR is shown in Figure 26.5. A comparison of three different methods (including CTEM) of measuring Seebeck coefficient at DLR is included. Two of them differ in holder geometry and temperature range but implement the same principle (difference in methodology: reversible vs. nonreversible temperature gradient) and use similar control software. The Seebeck values show an almost linear increase with temperature. The relatively small value of Seebeck coefficient for Pd is useful in determining the overall sensitivity of the apparatus, with noise becoming the limiting factor in resolving measurements near room temperature for the high temperature Seebeck apparatus (HT-S) of DLR. Both systems are in excellent agreement when also compared to literature data.<sup>76,77</sup> From the CTEM measurement it becomes obvious that thermal control of the sample chamber is crucial for high accuracy. Slow cooling down of the chamber yields best agreement to literature data whereas large temperature differences which arise during rapid heating before the measurement need time to decay before the measurement becomes reliable (Figure 26.5(b), scattering CTEM data near 500°C).

A further comparison in Seebeck coefficient measurements was made below 400 K, this time using constantan, between Cardiff's closed-loop He cryostat system, DLR's CTEM apparatus employing liquid  $\text{N}_2$  cooling, and the PPMS in Aarhus (see Figure 26.6). Below about 300 K, both Cardiff's and DLR's results agree very well to the literature values derived from standard thermocouple tables (T-type) and precision measurements on Cu. Above 100 K there is an increasing small systematic error of around 2 to 3  $\mu\text{V}$  between the literature values and the PPMS measurement. An increasing systematic divergence in DLR's CTEM values was noted above 280 K. The reason for this error may lie in the different temperature regime of the measurement in both temperature regions (slow warming up from low temperature; slow cooling down from high temperature to 280 K).

Measurements of electrical conductivity performed on NIST SRM stainless steel (SRM1460) are displayed in Figure 26.7. Again, the relatively low resistivity of the values for this material (compared to thermoelectric semiconductor materials) is a good test of the apparatus sensitivity. Measurements at NEDO Cardiff, DLR, and the PPMS system at Aarhus are shown against the certified values provided by NIST.<sup>74</sup> It is evident that all laboratories' facilities are in very good agreement with published values. The largest deviation from the NIST data is observed for the DLR apparatus with a maximum 4% smaller fitting curve of the conductivity values.

In Figure 26.8(a) is displayed the electrical resistivity of a hot-pressed skutterudite material,  $\text{Co}_4\text{Sb}_{11.91}\text{Te}_{0.09}$ .<sup>75</sup> Since the PPMS facility is primarily a low-temperature system, only a comparison of measurements in the region 300 to 400 K was possible (see inset). Whilst both the four-point probes of Cardiff and DLR show excellent agreement in measurements on the skutterudite (within 2%), a positive systematic error of around 7% was noted in the PPMS measurement. Such a constant deviation may be





**FIGURE 26.5** (a) Seebeck coefficient measurements on Pd foil at Cardiff and with various facilities at DLR. Literature data<sup>76,77</sup> are shown as a solid line. Repeatability of the CTEM was checked for measurement modes with ascending and descending sample temperature. (b) Percentage deviation from literature values.

explained by uncertainty in determining the exact voltage pick up wire spacing and sample dimensions when contacting PPMS samples. In the case of Cardiff and DLR, a fixed four-point probe head was used, thus minimizing such errors. A comparison for a second skutterudite sample— $(\text{Co}_{0.9}\text{Ni}_{0.1})_4\text{Sb}_{11.95}\text{Te}_{0.05}$  round-robin sample #1581 (Figure 26.8(b))—reveals again that both DLR and Cardiff measurements agree within 2 to 3%, yet there is a small systematic deviation in measurements performed by PPMS.

For standardization of thermal diffusivity measurements, again SRM1460 was used. An identical 8 mm disc sample was measured by both partners. A comparison is given with literature values,<sup>56</sup> measured also on a commercial Netzsch laser flash system for the same material and having been shown to be in agreement with certified thermal conductivity values provided by NIST (Figure 26.9).

Sensitivity of the infrared detection system employed in the laser flash apparatus increases with sample temperature. At room temperature, the signal-to-noise ratio is often low (especially with highly reflective materials). Both Cardiff and DLR measurements are in good agreement to published data, with DLR's and Henderson et al.'s commercial Netzsch LFA systems achieving somewhat better reproducibility around room temperature.

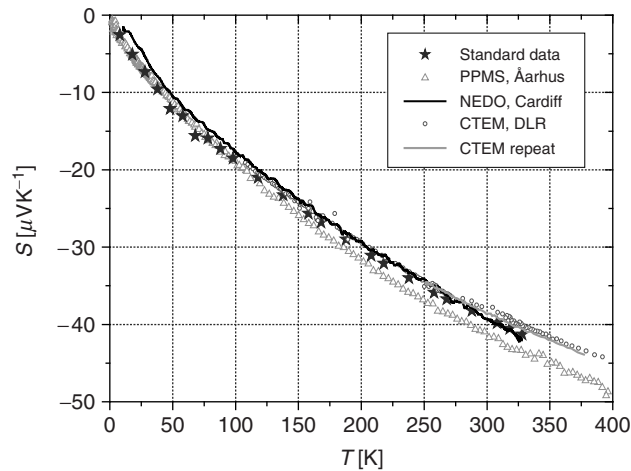


FIGURE 26.6 Seebeck coefficient measurements on constantan.

In obtaining thermal conductivity from thermal diffusivity measurements, it is necessary to measure the specific heat of the sample. While both Cardiff and DLR use a commercial DSC<sup>39</sup> for this purpose, the PPMS uses a somewhat different method of obtaining  $c_p$ . A comparison of specific heat measurements on skutterudite  $\text{CoSb}_3$  samples was made (Figure 26.10). It was noted that  $c_p$  may be considered independent of any small amounts of additional Ni and Te doping in these samples and hence a comparison was drawn from previous measurements made by each partner. Although not a true comparison for round-robin testing, it does identify any significant differences in the measuring systems. From its principle, and according to experience, DSC is the source of some uncertainty in the determination of the thermal conductivity in using a laser flash method. Both Cardiff samples and PPMS measurements show reasonably good agreement and are close to the expected constant theoretical value of 0.23 J/gK following Dulong Petits law. However, DLR measurements of  $c_p$  appear to fluctuate about

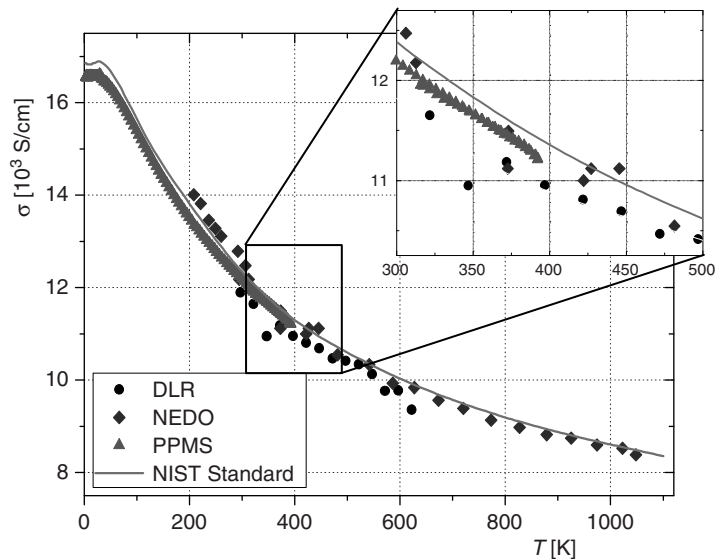
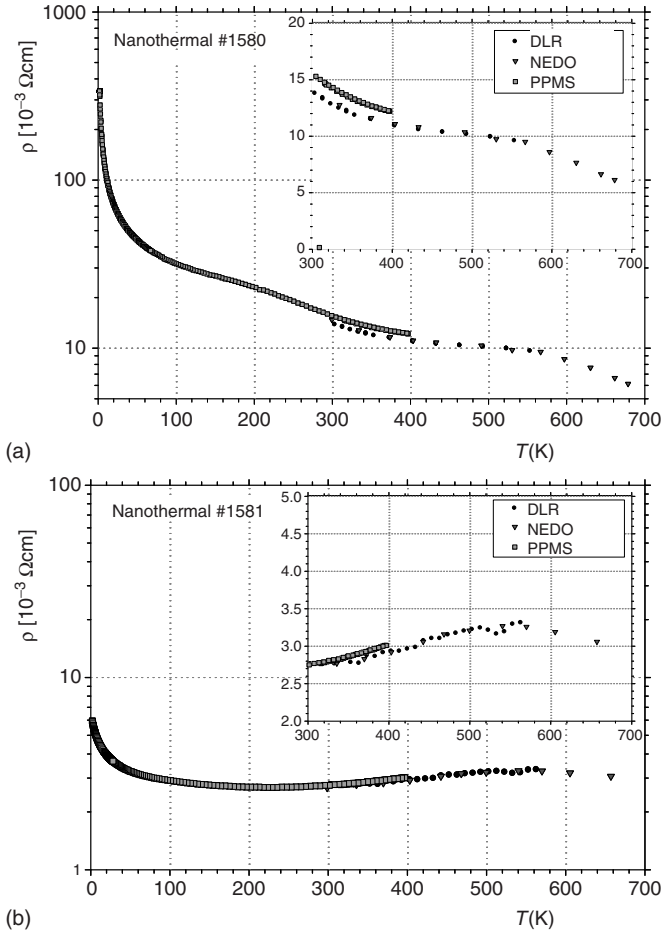
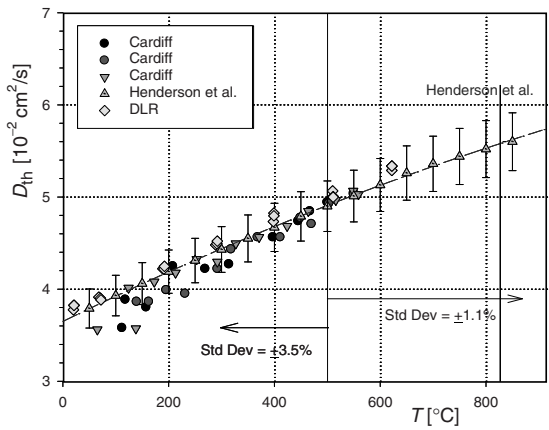


FIGURE 26.7 Electrical conductivity measurements on standard NIST stainless steel SRM1460.



**FIGURE 26.8** Electrical resistivity measurements on round-robin samples (a) #1580 ( $\text{Co}_4\text{Sb}_{11.91}\text{Te}_{0.09}$ ) and (b) #1581 ( $(\text{Co}_{0.9}\text{Ni}_{0.1})_4\text{Sb}_{11.95}\text{Te}_{0.05}$ ). The insets show the comparison in the temperature range 300 to 700 K.



**FIGURE 26.9** Thermal diffusivity measurements using laser flash method for SRM1460 Stainless Steel (NIST). Comparison is shown with published thermal diffusivity data. (Source: Henderson, J.B., Giblin, F., Blumm, J., and Hagemann, L., *Int. J. Thermophys.*, 19(6), 1647–1656, 1998. With permission.)

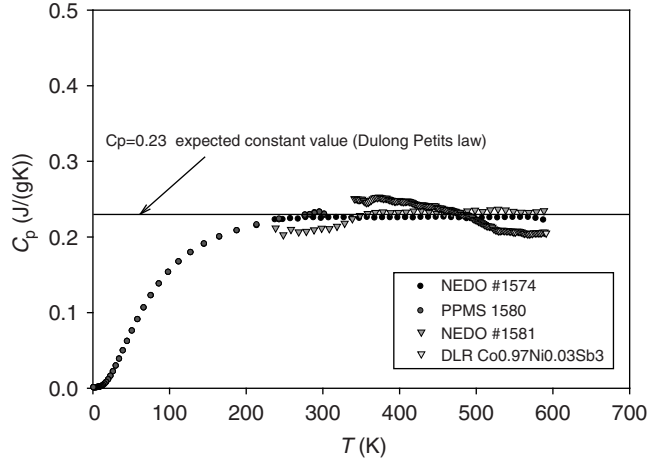


FIGURE 26.10 Specific heat measurements on CoSb<sub>3</sub> skutterudite samples.

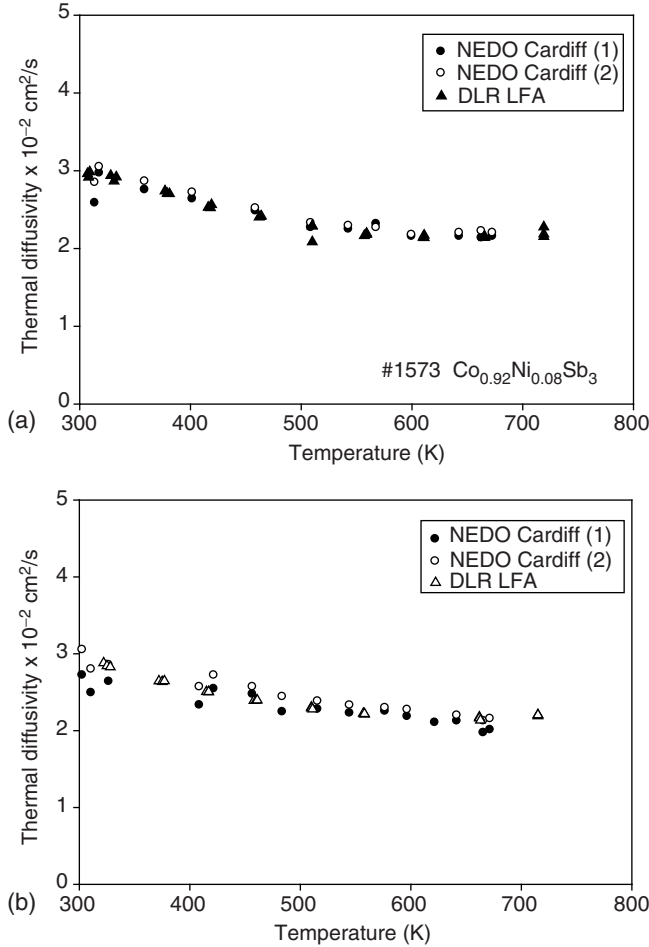


FIGURE 26.11 Round-robin tests for thermal diffusivity measurements using laser flash method: (a)  $\text{Co}_{0.92}\text{Ni}_{0.08}\text{Sb}_3$ ; (b)  $\text{Co}_{0.97}\text{Ni}_{0.03}\text{Sb}_3$ .

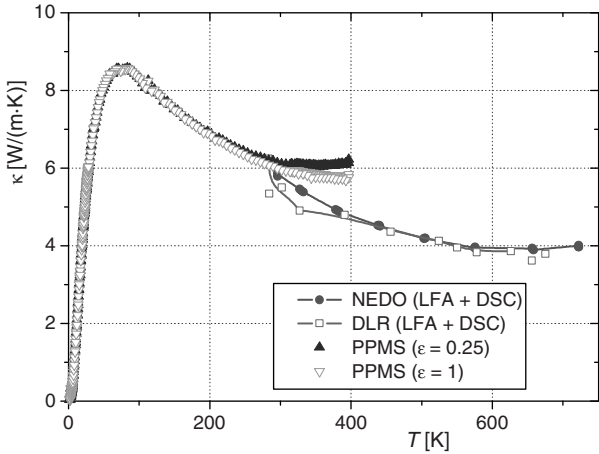


FIGURE 26.12 Round-robin measurement of thermal conductivity for  $\text{Co}_4\text{Sb}_{11.91}\text{Te}_{0.09}$  sample.

the expected theoretical value. The results at DLR were obtained with a simple plate-type sample holder whereas more specialized holder types for best  $c_p$  determination are accessible. Comparison of thermal diffusivity measurements on skutterudite  $\text{CoSb}_3$  materials was also performed using two round-robin samples, namely with 3 and 8% Ni doping as shown in Figure 26.11(a) and (b), respectively. Both sets of results show excellent agreement and are well within the estimated reproducibility of the facilities.

The PPMS facility is able to perform direct thermal conductivity measurements as described earlier. A comparison was therefore made with thermal conductivity data obtained through laser flash and specific heat measurements from DLR and Cardiff (see Figure 26.12). Although the PPMS system produces very little scatter, above 300 K there appears to be significant deviation from the Cardiff and DLR measured values. Further comparison of thermal diffusivity and thermal conductivity measurements between Cardiff and DLR would indicate that the PPMS thermal conductivity measurements between 300 and 400 K are in doubt and should be checked against a standard reference material.

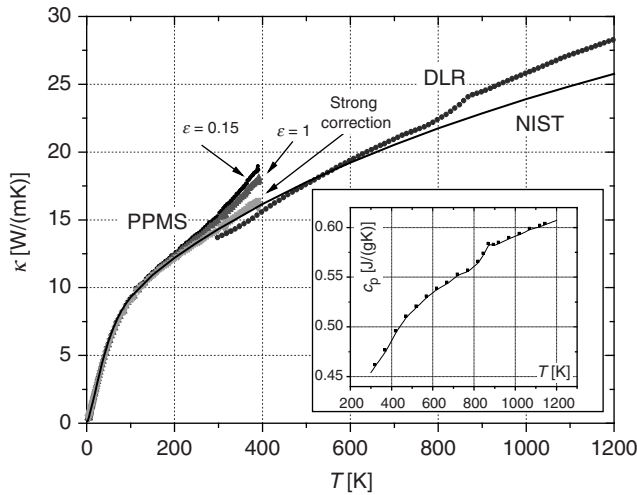


FIGURE 26.13 Comparison of direct measurement of the thermal conductivity of SRM1460 by PPMS to calculated values from thermal diffusivity (LFA, measured at DLR, see Figure 26.9) and specific heat (literature values<sup>56</sup> inset).

For this purpose, SRM1460 (Figure 26.13) was measured by PPMS. Again, an increasing deviation of the PPMS from the NIST data is observed above room temperature which might be understood as an underestimation of radiation losses. Strong overweighting of the according correction term leads to coincidence with the standard data. (The same large weighting factor was leading to coincidence of PPMS results in round-robin measurements also on zinc antimonide and skutterudites.) DLR data coincide well to the NIST SRM1460 standard up to temperatures of 800 K (maximum deviation of 5 to 6%). Above the anomaly which was reported by Henderson<sup>56</sup> but is not reflected by the NIST data, the DLR data increasingly deviate from the NIST data up to a difference of 8.6% at 1200 K.

## 26.4 Conclusions

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Evidently, there is a strong necessity for standardization procedures like round-robin and intralaboratory comparison of measuring apparatus. Typically, comparison between apparatus which are estimated as reliable reveals deviation of 5 to 10% for any thermoelectric properties: Seebeck coefficient, electrical conductivity, and thermal conductivity.

Available SRMs and precision literature data on thermoelectric properties have been compiled, demonstrating an evident lack of RM among thermoelectric materials of high performance. Technological problems in preparing homogeneous materials out of this group are one of the obstacles here. The suitability of a noncommon characterization technique, the SMP, which provides two-dimensional mappings of the Seebeck coefficient to monitor substantial information on functional homogeneity of thermoelectric materials has been shown. Simultaneous methods of thermoelectric measurements have been demonstrated to be a valuable instrument for thermoelectric standardization.

A comparison of thermoelectric transport properties has been made between NEDO Laboratories at Cardiff, U.K., and DLR Cologne, Germany. A comparison of this data has also been made against a commercial PPMS system at Århus University, Denmark. For calibration of electrical resistivity and thermal diffusivity measurements, a suitable certified reference material (SRM1460) was obtained from NIST. Seebeck coefficient measurements were compared against literature values using both constantan alloy and palladium metal foil. Intralaboratory tests were carried out at DLR involving alternative principles of thermoelectric measurements. Round-robin testing was made using skutterudite materials.

Seebeck measurements on Pd and constantan were in very good agreement with literature values. Increasingly above 100 K, PPMS showed a small deviation from the literature values up to 2 to 3  $\mu\text{V/K}$ . Measurements of electrical resistivity on SRM1460 show very close agreement with certified values from NIST. PPMS measurements were also in good agreement but are limited to a maximum temperature of 400 K. Round-robin electrical resistivity measurements made on skutterudite materials also indicate good agreement between Cardiff and DLR of around 2 to 3%, but a positive systematic error by PPMS of approximately 7%.

Thermal diffusivity measurements on SRM1460 are in good agreement ( $\sim 3\%$ ) with literature data. Agreement of this quality is further demonstrated by round-robin tests made on skutterudite material. A comparison of thermal conductivity measurements obtained indirectly from diffusivity and specific heat measurements with PPMS illustrates a significant error above room temperature in the PPMS which was confirmed by measurement of SRMs using PPMS.

Intralaboratory comparison between differing methods reveals methodologic results on measurement control and superior principles. The CTEM apparatus at DLR, capable to measure simultaneously the Seebeck coefficient, electrical conductivity, thermal conductivity, and figure-of-merit (Harman method) provides the highest accuracy of Seebeck measurements whereas thermal bypassing by thermal radiation limits the temperature range of accurate thermal conductivity determination up to about 300 to 400°C. It was shown that Seebeck measurements may reach high accuracy not only in temperature-stabilized mode but also in passive relaxation mode. Changing heating rates and temperature gradients due to controller oscillations are a stronger source of error than moderate



and stable temperature gradients inside the measuring chamber which form during slow passive temperature drift.

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